Analysis of the magnetic coupling in binuclear complexes. II. Derivation of valence effective Hamiltonians from *ab initio* CI and DFT calculations

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Most interpretations of the magnetic coupling J between two unpaired electrons rest upon simple valence models that involve essentially the ferromagnetic direct exchange contribution, K_{ab}, and the antiferromagnetic effect of the delocalization resulting from the interaction between neutral and ionic determinants, t_{ab}, whose energy difference is U. Ab initio valence-only calculations give very poor estimates of J, whatever the definition of the magnetic orbitals, and large CI expansions are required to evaluate it properly. It is, however, possible to define valence effective Hamiltonians from the knowledge of the eigenenergies and the eigenvectors of these accurate CI calculations. When applied to four different complexes, this strategy shows that spin polarization may change the sign of the direct exchange interaction, K_{ab}, and that dynamical correlation results in a dramatic reduction of the effective repulsion U. The present article also shows how K_{ab}, t_{ab}, and U effective parameters can be extracted from density functional theory (DFT) calculations and that the typical overestimation of J in DFT can be attributed to an excessive lowering of the effective on-site repulsion. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1446024]

I. INTRODUCTION

The magnetic properties of molecular biradicals, intermolecular complexes, transition metal binuclear, or polynuclear architectures are the subject of an intense research effort. In material science as well, magnetic lattices receive an increasing attention.[1–4] The basic characteristics of these systems, which all involve localized unpaired electrons, are the sign and the amplitude of the coupling J between the unpaired electrons on neighbor sites. This information may be introduced in a Heisenberg–Dirac–Van Vleck spin-only Hamiltonian:[5]

$$\hat{H} = -\sum_{i,j} J_{ij}\hat{S}_i\hat{S}_j, \tag{1}$$

where $\hat{S}_i$ and $\hat{S}_j$ are the spin operators on sites i and j. The experimental values of J are obtained by fitting the results coming from measurements of magnetic susceptibility, neutron scattering, or Raman spectroscopy to those obtained by assuming the Heisenberg microscopic Hamiltonian. The magnetic coupling constant J may be negative (antiferromagnetism, AF) or positive (ferromagnetism, F).[6] This coupling is essentially local.[7–9] The interaction between the nearest

neighbors usually prevails, although in some architectures the second neighbor interaction has been assumed to be similar to the nearest one as in $CuGeO_3$[10] and Li_2CuO_2.[11]

From the very beginning of this domain, models have been proposed which essentially rest upon a very limited set of electrons and orbitals. Most of them invoke the magnetic orbitals and the unpaired electrons only. Hence for a binuclear problem with $m_s = \pm \frac{1}{2}$ on each magnetic center, only two unpaired electrons in two local orbitals a and b are considered. The models may be formulated in a nonorthogonal valence bond (VB) model,[12,13] in an orthogonal valence bond description[14] if a and b have been orthogonalized, i.e., $\langle a|b\rangle = 0$, or in a valence configuration interaction (VCI) picture.[15] All these models stay on a minimal valence description of the problem. They have led to some qualitative conclusions:

(i) the direct exchange K_{ab} between the magnetic orbitals is a ferromagnetic (triplet favoring) contribution;

(ii) the other contribution is antiferromagnetic and comes from the specific electronic delocalization occurring in the singlet, through the mixing of the neutral dominant singlet VB configurations $(1/\sqrt{2})(a\bar{b}+b\bar{a})$ with

the ionic VB determinants $|a\bar{a}\rangle$ and $|b\bar{b}\rangle$. Its amplitude is governed by the effective hopping integral t_{ab}:

$$2t_{ab}=\left\langle \frac{1}{\sqrt{2}}(a\bar{b}+b\bar{a})\left|\hat{H}\right|\frac{1}{\sqrt{2}}(a\bar{a}+b\bar{b})\right\rangle \qquad (2)$$

and by the energy difference between the neutral and ionic VB structures:

$$U=\tfrac{1}{2}[\langle(a\bar{a}+b\bar{b})|\hat{H}|(a\bar{a}+b\bar{b})\rangle$$
$$-\langle(a\bar{b}+b\bar{a})|\hat{H}|(a\bar{b}+b\bar{a})\rangle]. \qquad (3)$$

Up to the second order, the antiferromagnetic contribution[14] to J is $-4t_{ab}^2/U$ and the quantity $2t_{ab}$ can be related to the energy difference between the symmetry-adapted g and u molecular orbitals:[15] $2t_{ab}=\varepsilon_g-\varepsilon_u$.

These models have been widely used not only as *a posteriori* rationalization of the experiment, for instance to interpret the structural dependence of J in a series of complexes,[16–18] but also as an intellectual guide, for instance, to build ferro- or ferrimagnetic lattices.[19]

However, *ab initio* calculations apparently fail to support the validity of these elementary pictures. It is actually possible to define accurate magnetic orbitals from self-consistent field (SCF) calculations on the upper or lower multiplets of a binuclear system. These calculations minimize the energy of a simple description of these states (in terms of two determinants for a two electron in two orbital problem) in a mean field approximation. Natural magnetic orbitals may as well be defined from very accurate descriptions, involving extensive configuration interaction (CI) expansions. But in both cases the valence-only description, i.e., the interaction between $|a\bar{b}\rangle$, $|b\bar{a}\rangle$, $|a\bar{a}\rangle$, and $|b\bar{b}\rangle$ determinants, gives very poor results, the values of J being frequently of incorrect sign and, when not, one order of magnitude too small.[20–25]

Accurate values of J can be obtained by *ab initio* CI techniques.[8,9,22–30] A perturbative second-order analysis was performed by Malrieu *et al.*[31–33] showing the importance of processes which involve other orbitals and electrons. Since the perturbation expansion is not very reliable due to convergence problems,[32] a selected CI scheme has been defined from perturbative arguments. The energies and wave functions of the desired states are obtained by diagonalizing different selected spaces. The dynamical correlation effect is obtained through excitations involving either occupied (holes, h) or virtual (particles, p) inactive orbitals. Up to the second order in a perturbative expansion, the excitation can concern at most two holes and two particles. These ($2h+2p$) excitations do not contribute to the energy difference and can be omitted in the CI expansion, leading to the variational so-called difference dedicated CI method.[34] This approach has led to very accurate values of the magnetic coupling in a wide series of systems. A preceding paper[35] has shown that it is possible to analyze the role of the various types of processes which go beyond the valence-only description (spin-polarization, dynamical repolarization of ionic VB structures, etc.) using different CI spaces.

The first aim of this work is to analyze whether it is possible to return from this complex picture to a simple valence space description, in which the interactions are no longer the bare ones imposed by the direct action of the Hamiltonian, but effective interactions incorporating the effects of external correlation. The theory of effective Hamiltonians is a tool for a rigorous concentration of the information.[36,37] Its principle is recalled in Sec. III. When applied to a two-electron in two-orbital problem it gives a dressed valence-only Hamiltonian. The comparison between the bare and the dressed valence-only Hamiltonians, obtained for a series of four binuclear complexes of Cu (II) ions (described in Sec. II), shows the action of the dynamical correlation, i.e., the modification of the K_{ab}, t_{ab}, and U parameters. Three strategies are employed for this concentration of information, namely,

(i)   the original theory of Bloch,[38] which uses information coming from four exact eigenstates, when available;

(ii)   an alternative formalism, which defines a Hermitian effective Hamiltonian, by using the Gram–Schmidt orthogonalization;[39] and

(iii)   the theory of intermediate effective Hamiltonians, proposed by Malrieu *et al.*,[40] which handles the two lowest eigenstates only.

All these methods lead to a consistent conclusion concerning a dramatic reduction of the effective on-site repulsion U as an effect of the dynamical polarization.

The second prospect of the present work concerns DFT calculations on magnetic complexes (Sec. IV). It is shown that it is possible to derive DFT evaluations of the integrals K_{ab}, t_{ab}, and U, from various solutions of the Kohn–Sham equations (closed shell singlet, restricted open shell triplet, and broken-symmetry singlet solutions). These calculations lead to an overestimation of the $|t_{ab}/U|$ ratio, compared to the best *ab initio* $|t_{ab}^{\text{eff}}/U^{\text{eff}}|$ value, resulting in a too large ionic VB component in the broken-symmetry solution. This explains the generally observed overestimation of J in these approaches. The key role of the exchange potential will be illustrated and discussed. Finally, Sec. V contains the conclusions of both papers.

II. DESCRIPTION OF THE SYSTEMS AND COMPUTATIONAL DETAILS

Four binuclear systems involving two d^9 Cu(II) centers i.e., two active electrons in two magnetic orbitals have been considered. The first one is a fragment of the CuO_2 square lattice of the La_2CuO_4 perovskite, which presents superconducting behavior after hole doping, while it is a two-dimensional antiferromagnetic lattice with $J\sim-1000$ cm^{-1} before doping ($J_{\text{exp}}=-1032\pm48$ cm^{-1}, -1081 ± 40 cm^{-1}).[41,42] A Cu_2O_7 cluster properly embedded in a set of pseudopotentials and point charges [Fig. 1(a)] has been used to represent this system. The remaining three examples come from chemistry, namely,

(i)   the $[Cu_2Cl_6]^{2-}$ complex in a planar geometry, Fig. 1(b), with a weak antiferromagnetic character ($J_{\text{exp}}=0,-40$ cm^{-1});[43]

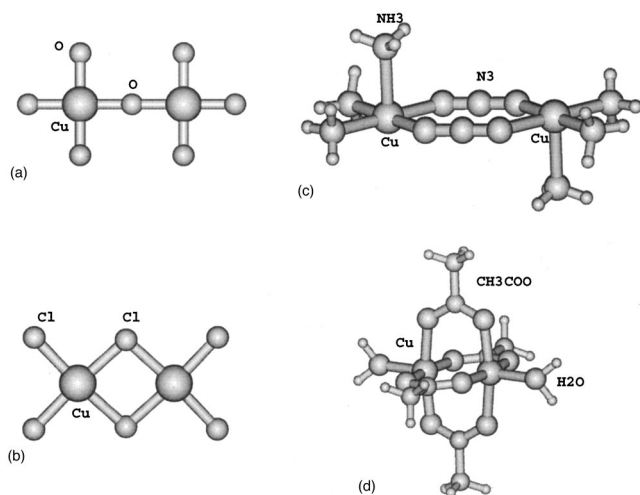FIG. 1. Schematic representation of the four models considered: (a) the Cu_2O_7 cluster; (b) the $[Cu_2Cl_6]^{2-}$ complex, in a planar geometry; (c) the $[Cu_2(\mu\text{-}N_3)_2(NH_3)_6]^{2+}$ complex with end-to-end bridging azido ligands; and (d) the $Cu_2(\mu\text{-}CH_3COO)_4(H_2O)_2$ molecule.

(ii)　$[Cu_2(N_3)_2(NH_3)_6]^{2+}$ with end-to-end bridging-azido groups, Fig. 1(c), leading to a very strong antiferromagnetic behavior $(J_{exp} < -800 \text{ cm}^{-1})$;[44]

(iii)　$Cu_2(CH_3COO)_4(H_2O)_2$ with four acetato bridges, Fig. 1(d), presenting an intermediate antiferromagnetism $(J_{exp} = -286, -294 \pm 4 \text{ cm}^{-1})$.[45,46]

The relative orientation of the magnetic orbitals in these four systems is presented in the Scheme:
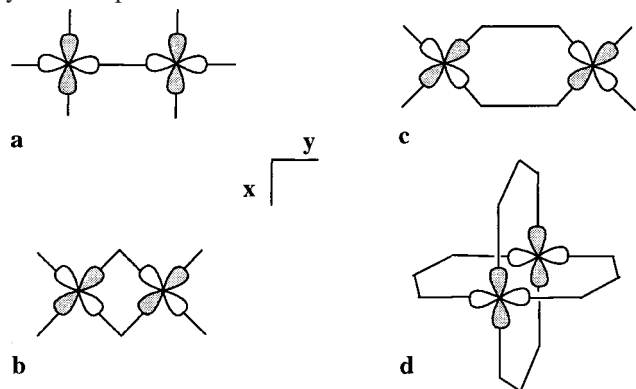
for (a) the Cu_2O_7 cluster, (b) the $[Cu_2Cl_6]^{2-}$ complex, (c) the $[Cu_2(N_3)_2(NH_3)_6]^{2+}$ complex, and (d) the $Cu_2(CH_3COO)_4(H_2O)_2$ molecule, respectively.

A more detailed description of these systems has been reported in paper I,[35] together with the computational details for the CI calculations. The MOLCAS 4.1 package[47] has been used to obtain the ROHF molecular orbitals. The CASDI program[48] has been used in the CI calculations and the NATURAL program[49] in the determination of the natural MOs.

All DFT calculations have been performed by means of the GAUSSIAN 98 code.[50] The B3LYP[51] parametrization has been used in the DFT calculations, with the following basis sets: for the $[Cu_2Cl_6]^{2-}$ and $[Cu_2(\mu\text{-}N_3)_2(NH_3)_6]^{2+}$ complexes, the Hay and Wadt core potential and basis functions have been used for copper atoms.[52] All electron basis sets

have been used for the remaining atoms, the 6-311G basis set for chlorine[53] and the 6-31G one for hydrogen and nitrogen atoms.[54] For the $Cu_2(\mu\text{-}CH_3COO)_4(H_2O)_2$ molecule, the effective core pseudopotential and basis functions proposed by Stevens, Basch, and Krauss[55] have been employed for the Cu, O, and C atoms. For the cuprate, the same basis functions as in the HF–CI calculations have been used for Cu and O atoms.

In order to analyze various aspects of the dynamical correlation, four different CI spaces are used, namely,

(i)　　the bare valence CAS (CASCI);
(ii)　　the DDCI1 space containing all the configurations reached by single excitations on the top of the CAS. Three types of excitations can be distinguished:

- $1h$, where an electron moves from an inactive occupied orbital to an active orbital, with a possible simultaneous single excitation inside the active space;
- $1p$, where an active electron is moved to a virtual orbital, and as in the preceding case, this movement can be coupled with single excitations inside the active space;
- $1h+1p$, where an electron moves from an occupied to a virtual orbital, with possible simultaneous single excitations inside the active space. The spin polarization contributions, i.e., a simultaneous excitation of a core electron to the active space and of an active electron of different spin to a virtual orbital, are included.

(iii)　　the DDCI2 space, which adds to the previous space the $2h$ determinants, i.e., two core electrons moving to the active orbitals, and $2p$ excitations, i.e., two electrons from the active orbitals to the virtual ones;
(iv)　　the DDCI space, containing also the $2h+1p$ determinants (two core electrons moving to an active orbital and to a virtual one, respectively) and $1h+2p$ determinants (one core and one active electrons moving to two virtual orbitals).

Regarding the DFT calculations, Noodleman's broken-symmetry approach[56] has been used to establish the value of the magnetic coupling. Since the overlap between the magnetic orbitals is rather small in all the studied systems (see Sec. IV B), the limit of strong orthogonality has been considered, J being calculated from

$$J = 2(E_{BS} - E_T), \qquad (4)$$

where E_{BS} and E_T are the unrestricted broken symmetry determinant and triplet state energies, respectively.

III. STRICT DETERMINATION OF VALENCE EFFECTIVE HAMILTONIANS FROM ACCURATE AB INITIO CI CALCULATIONS

A. The bare valence-only Hamiltonian

Let us recall briefly the nature of the model space, built from two orthogonal magnetic local orbitals, a and b. It is composed of four determinants, two neutral, $|a\bar{b}\rangle$ and $|b\bar{a}\rangle$, and two ionic ones, $|a\bar{a}\rangle$ and $|b\bar{b}\rangle$. The Hamiltonian expressed in this reduced complete active space takes the form

$$
\begin{array}{c}
|a\bar{b}\rangle \\
|b\bar{a}\rangle \\
|a\bar{a}\rangle \\
|b\bar{b}\rangle
\end{array}
\begin{bmatrix}
H_{NN} & K_{ab} & t_{ab} & t_{ab} \\
K_{ab} & H_{NN} & t_{ab} & t_{ab} \\
t_{ab} & t_{ab} & H_{NN}+U & K_{ab} \\
t_{ab} & t_{ab} & K_{ab} & H_{NN}+U
\end{bmatrix},
\tag{5}
$$

where H_{NN} is the energy of the neutral determinants. This space generates

(i)   a purely neutral triplet state $|T_u\rangle = (1/\sqrt{2})(|a\bar{b}\rangle - |b\bar{a}\rangle)$,

(ii)   a purely ionic singlet state of u symmetry $|S_u\rangle = (1/\sqrt{2})(|a\bar{a}\rangle - |b\bar{b}\rangle)$,

(iii)   two singlet states of g symmetry, $|S_g^1\rangle$ and $|S_g^2\rangle$, that may be expressed as linear combinations of a purely neutral singlet $|S_g^N\rangle = (1/\sqrt{2})(|a\bar{b}\rangle + |b\bar{a}\rangle)$, also denoted S_{ab} in paper I,[35] and a purely ionic singlet $|S_g^I\rangle = (1/\sqrt{2})(|a\bar{a}\rangle + |b\bar{b}\rangle)$.

The Hamiltonian can be expressed in the basis of $\hat{S}^2$ eigenvector configurations. Taking the energy of the triplet

$$
{}^3E_u = H_{NN} - K_{ab}
\tag{6}
$$

as the energy origin, the Hamiltonian can be written

$$
\begin{array}{c}
|S_g^N\rangle \\
|S_g^I\rangle \\
|T_u\rangle \\
|S_u\rangle
\end{array}
\begin{bmatrix}
2K_{ab} & 2t_{ab} & 0 & 0 \\
2t_{ab} & 2K_{ab}+U & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & U
\end{bmatrix}.
\tag{7}
$$

The $|S_u\rangle$ state lies at the energy U above the triplet state. In the g symmetry the lowest singlet state $|S_g^1\rangle = c_N|S_g^N\rangle + c_I|S_g^I\rangle$ (with $c_N > c_I > 0$) is essentially neutral. Its energy is

$$
{}^1E_g^1 = K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2}.
\tag{8}
$$

The second root $|S_g^2\rangle = -c_I|S_g^N\rangle + c_N|S_g^I\rangle$ is essentially ionic and much higher in energy:

$$
{}^1E_g^2 = K_{ab} + \frac{U + \sqrt{U^2 + 16t_{ab}^2}}{2},
\tag{9}
$$

lying close to U when $|t_{ab}| \ll U$.

Paper I of this series[35] has shown how to obtain the values of the K_{ab}, t_{ab}, and U integrals from the CASCI solution. A second-order perturbative expansion leads to the well-known expression of the magnetic coupling:[14]

$$
J = 2K_{ab} - \frac{4t_{ab}^2}{U}.
\tag{10}
$$

Using the relations $2t_{ab} = \varepsilon_g - \varepsilon_u$ and $U = E_I - E_N = J_{aa} - J_{ab}$ (J_{aa} and J_{ab} being the one and two-center Coulomb repulsions, respectively), Eq. (10) can be written as[15]

$$
J = 2K_{ab} - \frac{(\varepsilon_g - \varepsilon_u)^2}{J_{aa} - J_{ab}},
\tag{11}
$$

exploited in most of the qualitative rationalizations of the magnetic coupling and of its structural dependence.[16–18]

B. The effective Hamiltonian approach

Whatever the definition of the valence space (Hartree Fock or natural orbitals), the physics of the magnetic coupling cannot be contained in the two elementary features, namely direct exchange and kinetic exchange. It would be impossible as well to reduce it to an enlarged valence space including one or a few occupied MOs of the bridging ligand, as suggested by the two-band model, popular in solid state physics, since dynamical correlation phenomena involving virtual MOs appear to be crucial in the determination of the amplitude of the magnetic coupling. But it is possible to project the exact information obtained from the large CI calculations into the valence space, considered as a model space, using the rigorous theory of effective Hamiltonians. This is the scope of the present section.

1. Quasi-degenerate perturbation theory

A way to produce an effective Hamiltonian, spanned by a given model space $\mathbb{S}$, consists in using the well-known quasidegenerate perturbation theory.[38,57–59] This is at least a conceptual guide, as it was in the preceding paper,[35] to which we shall refer for the identification of the various effects. The second-order expression of the matrix elements of $\hat{H}_{eff}$ are given by

$$
\langle I|\hat{H}_{eff}^{(2)}|L\rangle = \langle I|\hat{H}|L\rangle + \sum_{|\alpha\rangle \notin \mathbb{S}} \frac{\langle I|\hat{H}|\alpha\rangle\langle\alpha|\hat{H}|L\rangle}{E_L^{(0)} - E_\alpha^{(0)}},
$$
$$
\forall I,L \in \mathbb{S},
\tag{12}
$$

where $\mathbb{S}$ is the model space and the denominator is the zeroth-order energy difference between the *right* component $|L\rangle$ of the matrix element and the outer space determinant $|\alpha\rangle$. From this formulation it is possible to identify which matrix elements are affected by the various perturbers $|\alpha\rangle$. It should be pointed out that the formalism is not Hermitian, as shown by Eq. (12). If $|I\rangle$ and $|L\rangle$ have different zeroth-order energies, as occurs in magnetic systems when one of them is a neutral determinant and the other an ionic determinant, then $\langle I|\hat{H}_{eff}^{(2)}|L\rangle \neq \langle L|\hat{H}_{eff}^{(2)}|I\rangle$. In particular, the consequence to be expected is the effect of the perturbers to be larger for the $\langle \text{neutral}|\hat{H}_{eff}^{(2)}|\text{ionic}\rangle$ than for the $\langle \text{ionic}|\hat{H}_{eff}^{(2)}|\text{neutral}\rangle$ effective hopping, since the energy denominators are larger in absolute value for the latter.

Returning to the developments of paper I,[35] some predictions can be made:

(i) The spin polarization correction directly affects K_{ab} since it couples $|I\rangle = |\text{core } a\bar{b}\rangle$ and $|L\rangle = |\text{core } b\bar{a}\rangle$ through the spin polarized $a_{\bar{a}}^+ a_{\bar{h}} a_p^+ a_a|\text{core } a\bar{b}\rangle$ determinant.

(ii) The $1h+1p$ determinants giving the $a_p^+ a_h a_{\bar{a}}^+ a_{\bar{b}}|\text{core } a\bar{b}\rangle$ intermediate states change the active part of the wave function and lead to

- a small second-order modification of K_{ab} due to the interaction between the two neutral VB determinants,

- a modification of t_{ab} due to the interaction between the neutral and ionic determinants, and

- a more important modification of U due to the polarization of the ionic forms, as shown in the Diagram:

J. Chem. Phys., Vol. 116, No. 10, 8 March 2002

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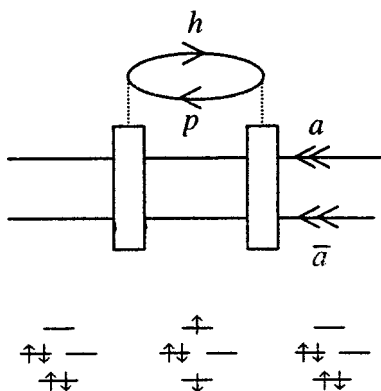
which may be seen as the internal part of Diagram 11 in paper I.[35] It gives

$$U^{\text{eff}} = U + \Delta U = U - \sum_h \sum_p \frac{\langle h | \tilde{J}_a - \tilde{J}_b | p \rangle^2}{U + \Delta E_{h \to p}}, \qquad (13)$$

where $\tilde{J}_a = J_a - K_a/2$ and $\Delta E_{h \to p}$ is the excitation energy to the $h \to p$ promotion.

The corrected kinetic exchange is obtained accordingly:

$$-\frac{t_{ab}^2}{U^{\text{eff}}}$$

$$= -\frac{t_{ab}^2}{U} \left(1 + \sum_h \sum_p \frac{\langle h | \tilde{J}_a - \tilde{J}_b | p \rangle^2}{U(U + \Delta E_{h \to p})} + \text{higher orders} \right). \qquad (14)$$

The fourth-order term was derived in the previous paper [Eq. (56) of Ref. 35]. The higher orders introduced by the change from U to U^{eff} are physical contributions to J through infinite summations of the diagrams.

(iii) The $2h$ and $2p$ excitations essentially consist in modifications of the exchange integral through the intermediate states $a_{\bar{a}}^+ a_{\bar{h}}^+ a_b^+ a_h | \text{core } a\bar{b} \rangle$ and $a_{\bar{p}}^+ a_{\bar{b}}^+ a_p^+ a_a | \text{core } a\bar{b} \rangle$;

(iv) the $2h+1p$ and $1h+2p$ determinants essentially touch the hopping integral up through the intermediate states $a_p^+ a_{h'}^+ a_{\bar{a}}^+ a_{\bar{h}} | \text{core } a\bar{b} \rangle$ and $a_{p'}^+ a_a a_p^+ a_{\bar{b}} | \text{core } a\bar{b} \rangle$.
To summarize this section, the expected results are

(a) the spin polarization should modify the K_{ab} value, the sign of the correction being system dependent; and

(b) the $1h+1p$ dynamical polarization of the ionic components should reduce the energy difference between the neutral and the ionic parts, U^{eff}. As shown in the Appendix, it may be predicted that at the third order the same perturbers should lower the $|\langle a\bar{a} | \Delta \hat{H}^{(3)} | a\bar{b} \rangle|$, i.e., the $|\langle \text{ionic} | \Delta \hat{H}^{(3)} | \text{neutral} \rangle| = |t_{IN}|$ value, while the $|\langle a\bar{b} | \Delta \hat{H}^{(3)} | a\bar{a} \rangle|$ element, that is the $|\langle \text{neutral} | \Delta \hat{H}^{(3)} | \text{ionic} \rangle| = |t_{NI}|$ counterpart, should be left practically unchanged, contributing to the non-Hermitian character of the effective Hamiltonian. The $2h+1p$ and $1h+2p$ determinants should affect essentially the hopping integrals, and paper I[35] has shown that the effect is an increase of the t_{ab} magnitude.

Of course the present discussion is based on low-order considerations and the construction of $\hat{H}_{\text{eff}}$ from the variational CI calculations may somewhat differ from second-order developments. Moreover, the QDPT expansion has no chance to converge when working with this four-dimensional space. Actually, some ligand to metal charge transfer (LMCT) states lie below the ionic $M^+ M^- |S_u\rangle$ and $|S_g^2\rangle$ states. These LMCT states act as intruders, resulting in small positive energy denominators and inducing the divergence of the series. Hence the QDPT arguments are purely qualitative.[60] We now go on to nonperturbative approaches using our variational calculations in order to build effective Hamiltonians.

2. Effective Hamiltonian from the exact spectrum

The theory developed by Bloch[38] establishes a procedure to define effective Hamiltonians, expanded in a low-dimensional model space, from the knowledge of the eigenenergies and eigenstates of the exact Hamiltonian.

Let us consider a model space, $\mathbb{S}$, of small dimension, i.e., spanned by n vectors $|\Phi_I\rangle$. Its projector is

$$\hat{P}_{\mathbb{S}} = \sum_{I \in \mathbb{S}} |\Phi_I\rangle \langle \Phi_I|. \qquad (15)$$

Here we are interested in a valence CAS, spanned by the four VB determinants $\mathbb{S} = \{|a\bar{b}\rangle, |b\bar{a}\rangle, |a\bar{a}\rangle, |b\bar{b}\rangle\}$, or their four combinations: $\mathbb{S} = \{|S_g^N\rangle, |S_g^I\rangle, |S_u\rangle, |T_u\rangle\}$.

Suppose we know a large number of eigensolutions of the exact Hamiltonian:

$$\hat{H} |\Psi_k\rangle = E_k |\Psi_k\rangle. \qquad (16)$$

Consider now the n eigenvectors of $\hat{H}$ having the largest components (or projections) in the model space $\mathbb{S}$. These eigenvectors define a target space, $\mathbb{S}^T$, isodimensional to $\mathbb{S}$:

$$\hat{P}_{S^T} = \sum_{k \in S^T} |\Psi_k\rangle \langle \Psi_k|. \qquad (17)$$

The wave operator $\hat{\Omega}$ sends $\mathbb{S}$ to $\mathbb{S}^T$, $\hat{P}_{S^T} = \hat{\Omega} \hat{P}_{\mathbb{S}}$. We would like to define an effective Hamiltonian in $\mathbb{S}$, the eigensolutions of which are the most exact and informative. This means that we want an effective Hamiltonian:

$$\hat{H}_{\text{eff}} = \hat{P}_{\mathbb{S}} \hat{H}_{\text{eff}} \hat{P}_{\mathbb{S}}, \qquad (18)$$

such that its n eigenvalues are exact, and that its eigenvectors are projections of the corresponding exact eigenvectors in the model space:

$$\hat{H}_{\text{eff}}^{\text{Bloch}} |\hat{P}_{\mathbb{S}} \Psi_k\rangle = E_k |\hat{P}_{\mathbb{S}} \Psi_k\rangle. \qquad (19)$$

This is the definition of the Bloch effective Hamiltonian.[38] Since the projections of the (necessarily orthogonal) eigenvectors may be nonorthogonal,

$$S_{kl} = \langle \hat{P}_{\mathbb{S}} \Psi_k | \hat{P}_{\mathbb{S}} \Psi_l \rangle \neq 0 \quad \text{for } k \neq l, \qquad (20)$$

the Bloch effective Hamiltonian may be non-Hermitian.[61] It is more convenient to orthogonalize the $|\hat{P}_{\mathbb{S}} \Psi_k\rangle$ vectors by a procedure that modifies them as little as possible. The $S^{-1/2}$ transformation,

$$|\Psi_k'\rangle = S^{-1/2}|\hat{P}_S\Psi_k\rangle. \tag{21}$$

presents such a property and leads to the des Cloizeaux effective Hamiltonian:[57]

$$\hat{H}_{\text{eff}}^{\text{dC}}|\Psi_k'\rangle = E_k|\Psi_k'\rangle. \tag{22}$$

Other orthogonalizations are possible, for instance the Gram–Schmidt one[39] that is used hereafter.

Of course the previous developments are applicable when using an approximate spectrum of $\hat{H}$, resulting, for instance, from truncated CI calculations. Let us specify this technique in our two-electron/two-orbital problem. The model space being split into three subspaces of different spin and space symmetry, as shown previously, the effective Bloch Hamiltonian can only take the following form, taking as zero of energy the triplet state one:

$$
\begin{array}{c}
|S_g^N\rangle \\
|S_g^I\rangle \\
|T_u\rangle \\
|S_u\rangle
\end{array}
\begin{vmatrix}
2K_{ab}^B & 2t_{NI}^B & 0 & 0 \\
2t_{IN}^B & U^B+2K_{ab}^B & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & U^B+2(K_{ab}^B-K_{ab}'^B)
\end{vmatrix} = \hat{H}_{\text{eff}}^{\text{Bloch}}, \tag{23}
$$

where

$$K_{ab}^B = \langle a\bar{b}|\hat{H}_{\text{eff}}^{\text{Bloch}}|b\bar{a}\rangle, \tag{24}$$

$$K_{ab}'^B = \langle a\bar{a}|\hat{H}_{\text{eff}}^{\text{Bloch}}|b\bar{b}\rangle, \tag{25}$$

$$t_{NI}^B = \langle a\bar{b}|\hat{H}_{\text{eff}}^{\text{Bloch}}|a\bar{a}\rangle, \tag{26}$$

$$t_{IN}^B = \langle a\bar{a}|\hat{H}_{\text{eff}}^{\text{Bloch}}|a\bar{b}\rangle, \tag{27}$$

and

$$U^B = \langle a\bar{a}|\hat{H}_{\text{eff}}^{\text{Bloch}}|a\bar{a}\rangle - \langle a\bar{b}|\hat{H}_{\text{eff}}^{\text{Bloch}}|a\bar{b}\rangle + K_{ab}'^B - K_{ab}^B. \tag{28}$$

This Hamiltonian is non-Hermitian,

$$t_{NI}^B \neq t_{IN}^B, \tag{29}$$

and introduces five integrals: t_{NI}^B, t_{IN}^B, U^B, K_{ab}^B, and $K_{ab}'^B$. The projections of the eigenvectors $|^3\Psi_u\rangle$ and $|^1\Psi_u\rangle$ onto the model space are fixed by symmetry. It is not the case for the singlet states $|^1\Psi_g^1\rangle$ and $|^1\Psi_g^2\rangle$, whose projections in the model space have a degree of freedom, namely the ratio of the coefficients on $|S_g^N\rangle$ and $|S_g^I\rangle$:

$$|\hat{P}_S{}^1\Psi_g^1\rangle = c_N|S_g^N\rangle + c_I|S_g^I\rangle, \quad c_N > c_I > 0,$$
$$|\hat{P}_S{}^1\Psi_g^2\rangle = -c_N'|S_g^N\rangle + c_I'|S_g^I\rangle, \quad c_I' > c_N' > 0. \tag{30}$$

Hence the knowledge of the energy of the four states, ^3E_u, ^1E_u, $^1E_g^1$, and $^1E_g^2$, and of the two c_I/c_N and c_I'/c_N' ratios fixes univocally the values of the five parameters of the Bloch effective Hamiltonian.

Let us define the overlap between the projections of the two singlet states as

$$s = \langle \hat{P}_S{}^1\Psi_g^1|\hat{P}_S{}^1\Psi_g^2\rangle = -c_Nc_N' + c_Ic_I'. \tag{31}$$

The overlap matrix takes the form

$$S = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}. \tag{32}$$

The biorthogonal vectors are defined by

$$|\hat{P}_S\Psi_k^\dagger\rangle = S^{-1}|\hat{P}_S\Psi_k\rangle, \tag{33}$$

which for the case of the projections $|\hat{P}_S{}^1\Psi_g^1\rangle$ and $|\hat{P}_S{}^1\Psi_g^2\rangle$ become

$$|\hat{P}_S{}^1\Psi_g^{1\dagger}\rangle = \frac{1}{1-s^2}(|\hat{P}_S{}^1\Psi_g^1\rangle - s|\hat{P}_S{}^1\Psi_g^2\rangle),$$

$$|\hat{P}_S{}^1\Psi_g^{2\dagger}\rangle = \frac{1}{1-s^2}(-s|\hat{P}_S{}^1\Psi_g^1\rangle + |\hat{P}_S{}^1\Psi_g^2\rangle). \tag{34}$$

Using the spectral representation of the effective Hamiltonian,

$$H_{\text{eff}}^{\text{Bloch}} = \sum_{i=1,4} |\hat{P}_S\Psi_i\rangle E_i \langle \hat{P}_S\Psi_i^\dagger|, \tag{35}$$

it is possible to extract the expression for the five effective parameters t_{NI}^B, t_{IN}^B, U^B, K_{ab}^B, and $K_{ab}'^B$:

$$2t_{NI}^B = \frac{1}{1-s^2}[^1E_g^1(c_Nc_I - sc_Nc_I') + {}^1E_g^2(sc_N'c_I - c_N'c_I')],$$

$$2t_{IN}^B = \frac{1}{1-s^2}[^1E_g^1(c_Nc_I + sc_N'c_I) - {}^1E_g^2(sc_Nc_I' + c_N'c_I')],$$

$$U^B = \frac{1}{1-s^2}[^1E_g^1(c_I^2 - c_N^2 - s(c_I'c_I + c_Nc_N'))$$
$$+ {}^1E_g^2(c_I'^2 - c_N'^2 - s(c_I'c_I + c_Nc_N'))], \tag{36}$$

$$2K_{ab}^B = \frac{1}{1-s^2}[^1E_g^1(c_N^2 + sc_Nc_N') + {}^1E_g^2(c_N'^2 + sc_Nc_N')] - {}^3E_u,$$

$$2K_{ab}'^B = \frac{1}{1-s^2}[^1E_g^1(c_I^2 - sc_Ic_I') + {}^1E_g^2(c_I'^2 - sc_I'c_I)] - {}^1E_u.$$

The exchange $K_{ab}'^B$ is different from K_{ab}^B, but for simplicity, its value will not be reported nor discussed hereafter.

Let us consider now the procedure to obtain a Hermitian effective Hamiltonian. The $S^{-1/2}$ orthogonalization of the eigenvectors projector onto the model space, leading to the des Cloizeaux effective Hamiltonian, symmetrically affects the essentially neutral state $|^1\Psi_g^1\rangle$, and the mostly ionic state $|^1\Psi_g^2\rangle$. Since we are mainly interested in the lowest (neutral) singlet, it is preferable to leave $|\hat{P}_S{}^1\Psi_g^1\rangle$ unchanged, and to orthogonalize $|\hat{P}_S{}^1\Psi_g^2\rangle$ (the projections of the ionic eigenstate) to $|\hat{P}_S{}^1\Psi_g^1\rangle$. This is a Gram–Schmidt orthogonalization. The second eigenvector has to satisfy $\langle \hat{P}_S{}^1\Psi_g^{2\dagger}|\hat{P}_S{}^1\Psi_g^1\rangle = 0$, and thus

$$c_N' = c_I, \quad c_I' = c_N,$$

$$|\hat{P}_S{}^1\Psi_g^{2\dagger}\rangle = -c_I|S_g^N\rangle + c_N|S_g^I\rangle \tag{37}$$

TABLE I. Magnetic coupling (J), ionic/neutral ratio of the ground state (c_I/c_N), and effective parameters (t_{ab}, K_{ab}, and U) for the Cu$_2$O$_7$ fragment of the La$_2$CuO$_4$ lattice from CI and B3LYP calculations. All the values in cm^{-1}, except U which is in eV. For the CI calculations, the CASCI and the DDCI lists of determinants have been employed, with two sets of orbitals (ROHF and natural orbitals). The CI parameters have been obtained by using the three kinds of effective Hamiltonians: Bloch, Gram–Schmidt (GS), and intermediate (Int).

MOs	Level	J^{a}	c_I/c_N	H_{eff}	U	$2K_{ab}$	t_{ab}	
ROHF	CASCI	−255	0.041		24.12	67		−3960
	DDCI	−1077	0.118	Bloch	7.24	581	t_{IN}	−3541
							t_{NI}	−7041
				GS	7.44	−229		−3589
				Int	8.21	−139		−3960
Natural	CASCI	−451	0.070		19.65	334		−5589
	DDCI	−1136	0.136	Bloch	7.21	339	t_{IN}	−4057
							t_{NI}	−5412
				GS	7.31	−22		−4089
				Int	9.98	386		−5589
B3LYP		−1689	0.230		4.20	108		−3903

$^{\text{a}}J_{\text{exp}}$: -1032 ± 48 cm^{-1}, -1081 ± 40 cm^{-1}, from Refs. 41 and 42.

is the second eigenvector of the Gram–Schmidt effective Hamiltonian $\hat{H}_{\text{eff}}^{GS}$, with $^1E_g^2$ as eigenenergy. This effective Hamiltonian takes the form

$$
\begin{array}{c}
|S_g^N\rangle \\
|S_g^I\rangle \\
|T_u\rangle \\
|S_u\rangle
\end{array}
\left[
\begin{array}{cccc}
2K_{ab}^{GS} & 2t_{ab}^{GS} & 0 & 0 \\
2t_{ab}^{GS} & U^{GS}+2K_{ab}^{GS} & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & U^{GS}+(2K_{ab}^{GS}-2K_{ab}^{GS})
\end{array}
\right]
$$

$$= \hat{H}_{\text{eff}}^{GS}. \tag{38}$$

This Hermitic Hamiltonian only introduces four parameters. The knowledge of the three energy differences and of the c_I/c_N ratio is sufficient to determine the values of these parameters. Since in this case the overlap between $|\hat{P}_S\,^1\Psi_g^1\rangle$ and $|\hat{P}_S\,^1\Psi_g^{2\dagger}\rangle$ is zero, as follows from Eqs. (30) and (37), we obtain the relations

$$2t_{ab}^{GS} = c_I c_N (^1E_g^1 - {}^1E_g^2),$$

$$U^{GS} = (c_I^2 - c_N^2)(^1E_g^1 - {}^1E_g^2), \tag{39}$$

$$2K_{ab}^{GS} = c_N^2\,{}^1E_g^1 + c_I^2\,{}^1E_g^2 - {}^3E_u.$$

In practice it is more convenient to write the projection of the ground singlet state $|\hat{P}_S\,^1\Psi_g^1\rangle$ in terms of the $|g\bar{g}\rangle$ and $|u\bar{u}\rangle$ symmetry-adapted valence determinants:

$$|\hat{P}_S\,^1\Psi_g^1\rangle = \lambda|g\bar{g}\rangle - \mu|u\bar{u}\rangle, \quad \lambda > \mu > 0, \tag{40}$$

where

$$c_N = \frac{\lambda+\mu}{\sqrt{2}} \quad \text{and} \quad c_I = \frac{\lambda-\mu}{\sqrt{2}}. \tag{41}$$

Equation (39) can be written as

$$2t_{ab}^{GS} = \tfrac{1}{2}(\lambda^2 - \mu^2)(^1E_g^1 - {}^1E_g^2),$$

$$U^{GS} = -2\lambda\mu(^1E_g^1 - {}^1E_g^2), \tag{42}$$

$$2K_{ab}^{GS} = \lambda\mu(^1E_g^1 - {}^1E_g^2) + \tfrac{1}{2}(^1E_g^1 + {}^1E_g^2) - {}^3E_u.$$

3. Numerical results

a. The Bloch effective Hamiltonian. Table I contains the Bloch effective Hamiltonian obtained from either ROHF orbitals (ROHF MOs) or natural orbitals (NOs) using the DDCI wave functions for the Cu$_2$O$_7$ fragment of the perovskite lattice. Figure 2 shows the effective parameters t_{NI}^B, t_{IN}^B, U^B, and K_{ab}^B and the c_I/c_N ratio obtained for this system by using increasingly correlated CI wave functions. When using ROHF MOs, several features are relevant:

(i) The bare K_{ab}^B value is small and important changes appear at the DDCI level.

(ii) The non-Hermiticity is important: $(t_{NI}^B - t_{IN}^B)/(t_{NI}^B + t_{IN}^B) \approx 20\% - 30\%$ and $|t_{NI}^B| > |t_{IN}^B|$, as expected, at all post-CASCI level. Figure 2 shows that $|t_{IN}^B|$ begins to decrease due to third-order effects related with the $1h+1p$ excitations (DDCI1) as explained in the Appendix. As shown from QDPT (already in paper I[35]) the $2h+1p$ perturbers appearing at the DDCI level enhance the effective $|t_{ab}^B|$ value.

(iii) The dominant effect is the drastic decrease of U^B, reduced to 30% of its bare value by the effect of the dynamical polarization ($1h+1p$, DDCI1).

Table I and Fig. 2 (bottom) show that NOs significantly change the zeroth-order values (larger K_{ab}^B, larger $|t_{ab}^B|$, smaller U^B at the CASCI level, due to larger delocalization tails in the magnetic orbitals[62]), but the trends are similar and the final DDCI effective interactions are very close (same value of U^B, same value of the product $t_{NI}^B \cdot t_{IN}^B$).

b. The Gram–Schmidt effective Hamiltonian. In order to avoid the uncomfortable non-Hermiticity problem, the Gram–Schmidt effective Hamiltonians are given for three systems: the cuprate cluster (Table I, Fig. 2), the chloride complex (Table II, Fig. 3), and the azido complex (Table III, Fig. 4). The case of copper acetate is discussed at the end of the section. As in Table I, Tables II and III contain the final DDCI results for the choride and azido systems, while as in Fig. 2, Figs. 3 and 4 also report values obtained from shorter CI expansions. The conclusions are quite similar to the preceding ones:

(i) The K_{ab}^{GS} effective exchange may become negative. This change of sign may be correlated with the sign of the spin polarization contribution, which is antiferromagnetic in the cuprate and the azido complex (cf. paper I[35]), but the changes in K_{ab}^{GS} are larger than the spin polarization contribution to J. Hence, the spin polarization is only a part of the effects contributing to K_{ab}.

(ii) When starting from ROHF MOs (top of figures), the $|t_{ab}^{GS}|$ value decreases under the effect of the $1h+1p$ determinants (compare CASCI and DDCI1 in Figs. 2–4) and raises close to the original CASCI value at
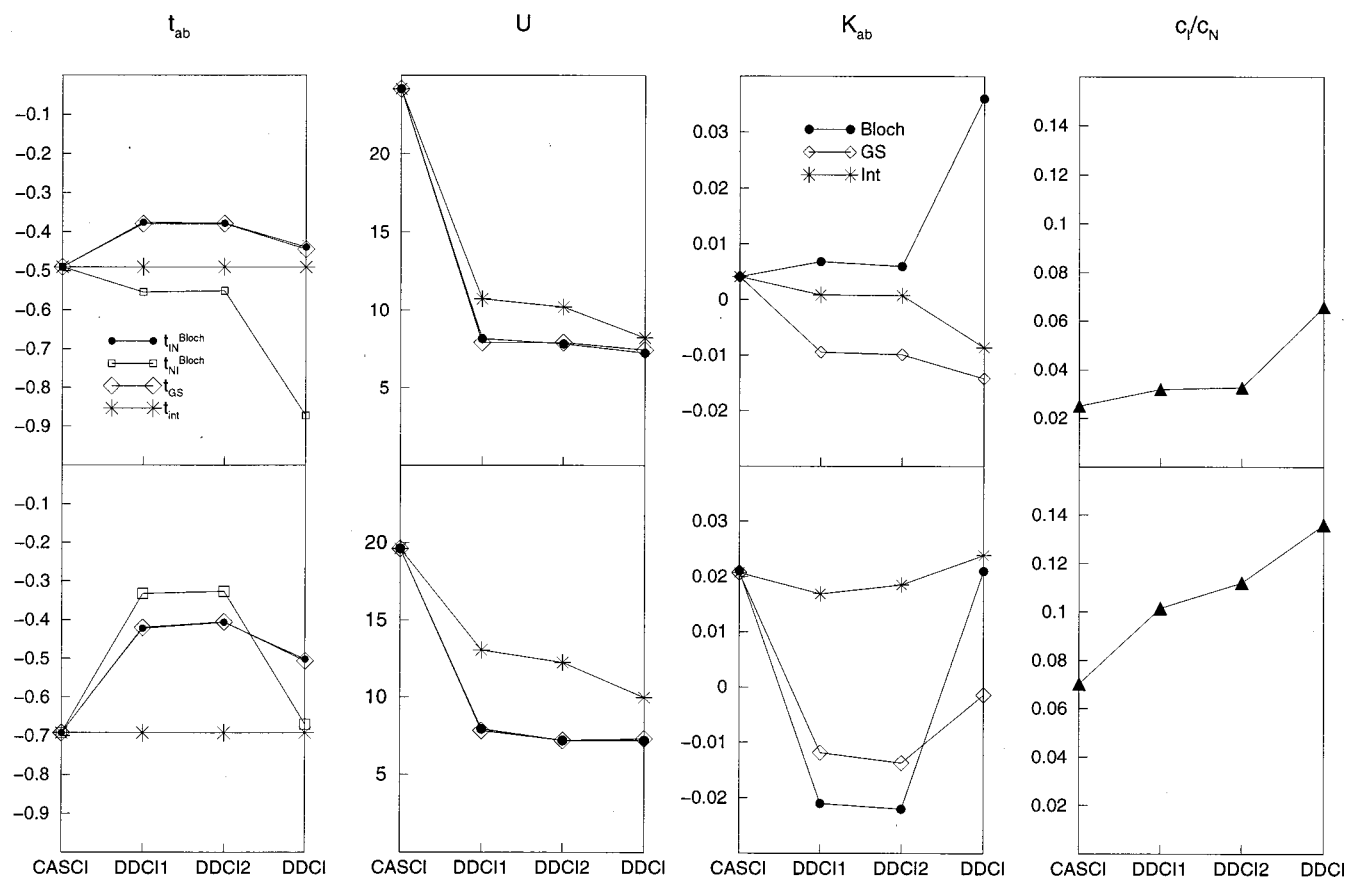
FIG. 2. Effective parameters t_{ab}, K_{ab}, and U (in eV) and ionic/neutral ratio (c_I/c_N) in the ground state wave function obtained for the Cu_2O_7 cluster from increasingly correlated CI wave function. Three types of effective Hamiltonians: Bloch, Gram–Schmidt (GS), and intermediate (Int) have been used and two different sets of molecular orbitals, ROHF (on the top) and natural orbitals (on the bottom), have been considered.

the DDCI level under the effect of the $2h+1p$ and $1h+2p$ determinants. When starting from NOs (bottom of figures), the CASCI value of $|t_{ab}^{GS}|$ is much larger. It is again reduced by the $1h+1p$ effects and slightly raises under the effects of the $2h+1p$ and

TABLE II. Magnetic coupling (J), ionic/neutral ratio of the ground state (c_I/c_N), and effective parameters (t_{ab}, K_{ab}, and U) for the $[Cu_2Cl_6]^{-2}$ complex. For the CI calculations, the CASCI and the DDCI lists of determinants have been employed, with two sets of orbitals (ROHF and natural orbitals). The CI parameters have been obtained by using the Gram–Schmidt (GS) and the intermediate (Int) effective Hamiltonians. All values in cm^{-1}, except for U, which is in eV.

MOs	Level	J[a]	c_I/c_N	H_{eff}	U	$2K_{ab}$	t_{ab}
ROHF	CASCI	11	0.009		23.61	27	−878
	DDCI	−22	0.042	GS	5.07	49	−853
				Int	5.22	52	−878
Natural	CASCI	78	0.024		18.32	162	−1764
	DDCI	−15	0.056	GS	5.07	113	−1145
				Int	7.81	182	−1764
B3LYP		−99	0.122		2.15	161	−1062

[a]J_{exp}: 0, −40 cm^{-1}, from Ref. 43.

$1h+2p$ excitations. The DDCI value with NOs is intermediate between the zeroth-order values (CASCI) of $|t_{ab}|$ from ROHF MOs and NOs.

(iii)   From both sets of orbitals, the main effect is the dramatic decrease of U^{GS} to 5 eV in $[Cu_2Cl_6]^{2-}$ and 7.5 eV in the cuprate. This decrease is essentially due to the $1h+1p$ excitations (dynamical repolarization of ionic VB structures).

For the azido complex the results have to be considered with caution since the identification of the essentially ionic valence $|^1\Psi_g^2\rangle$ state was quite difficult and ambiguous. For instance, at the DDCI2 level with NOs, two states, which are the 14th and 24th of their symmetry, have practically equal weights on the $|S_g^I\rangle$ configuration. At the DDCI level, the identification of the pertinent roots was impossible when using ROHF MOs. The rather arbitrary choice between them leads to very different effective integrals. There are a large number of ligand to metal or metal to ligand charge transfer states that can have lower energy than the metal to metal charge transfer, i.e., the ionic valence-bond state, which explains the high rank of the $|^1\Psi_g^2\rangle$ state. The same is true for the $|^1\Psi_u\rangle$ ionic state. A strong mixing between LMCT and ionic states can occur, which results in the difficult assignment of the predominantly valence ionic states. For the acetato complex the identification of these states happened to
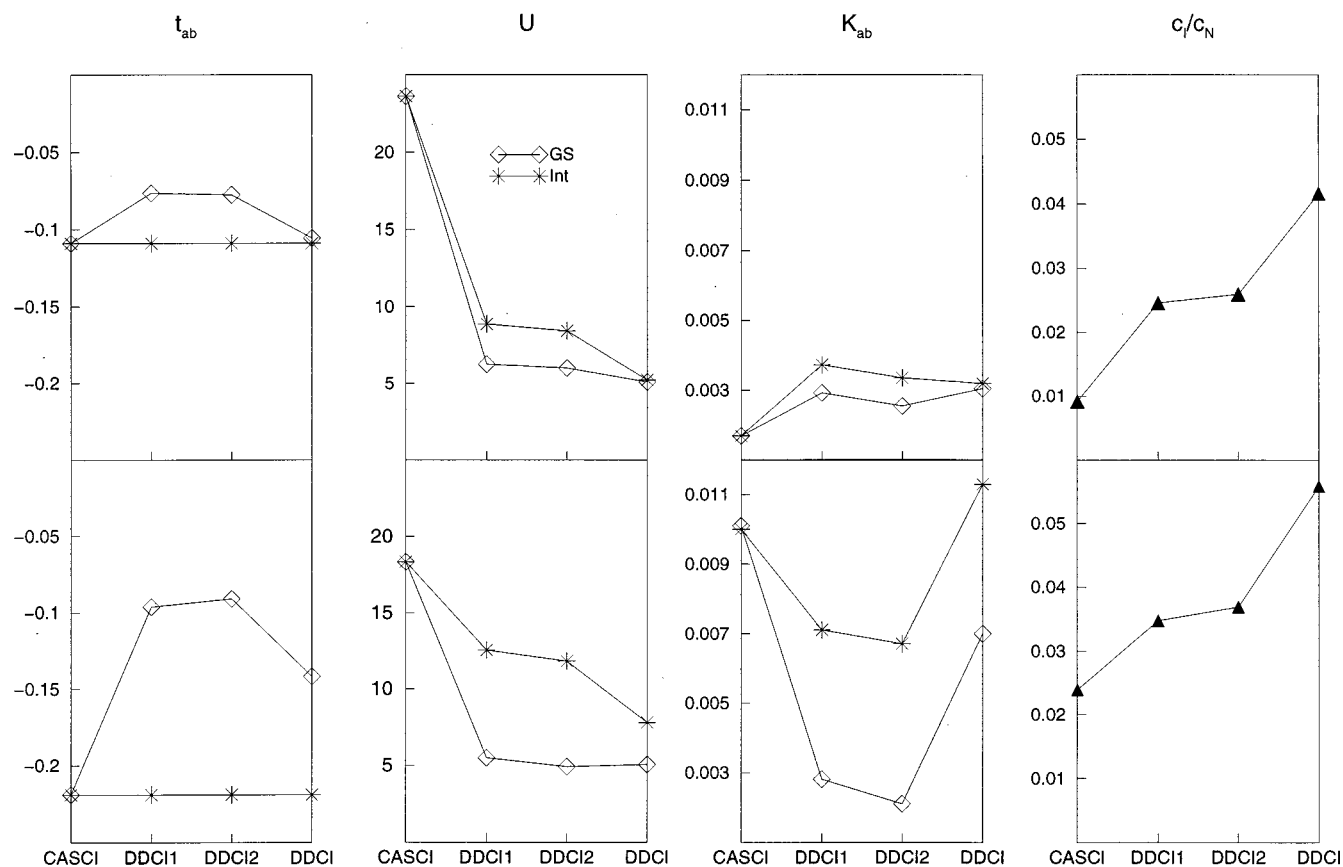
FIG. 3. Effective parameters t_{ab}, K_{ab}, and U (in eV) and ionic/neutral ratio (c_I/c_N) in the ground state wave function obtained for the $[Cu_2Cl_6]^{2-}$ complex from increasingly correlated CI wave function. The Gram–Schmidt and intermediate effective Hamiltonians have been used and two different sets of molecular orbitals, ROHF (on the top) and natural orbitals (on the bottom), have been considered.

be technically difficult, the ionic states being out of the first 25 lowest roots of the corresponding symmetry.

These remarks illustrate the conceptual limit of the strict effective Hamiltonian approach when the model space generates a set of eigenstates with a broad energy spectrum. In such a case intruder states appear. Their impact is not simply the divergent behavior of the QDPT, as usually believed. The intruder states result in an impossible or arbitrary definition

of the target space, i.e., of the set of the exact eigenvectors which are supposed to be generated from the model space. This comment supports the idea that one has to define less ambitious effective Hamiltonians, which, in this case, no longer try to generate the ionic excited states and concentrate on the two low-lying magnetic states. Such effective Hamiltonians may be defined using the concept and theory of the intermediate effective Hamiltonians.

C. Valence intermediate effective Hamiltonian

1. Theory

The intermediate Hamiltonian,[40] built on an n-dimensional model space, is only asked to reproduce $m(m<n)$ exact eigenvalues and the projections of the corresponding m eigenstates onto the model space:

$$\hat{H}^{\text{int}}|\hat{P}_S\Psi_k\rangle = E_k|\hat{P}_S\Psi_k\rangle, \quad k=1, \ m<n. \quad (43)$$

This imposes $m(m-1)$ conditions and there is an intrinsic flexibility in the definition of $\hat{H}^{\text{int}}$. When only the k state is looked for, it is possible to impose

$$\hat{H}^{\text{int}} = \hat{P}_S\hat{H}\hat{P}_S + \hat{P}_S\hat{\Delta}^k\hat{P}_S, \quad (44)$$

where $\hat{\Delta}^k$ is a state specific diagonal operator. For the particular determinant $|I\rangle$ of the model space, the eigenequations for the exact Hamiltonian lead to
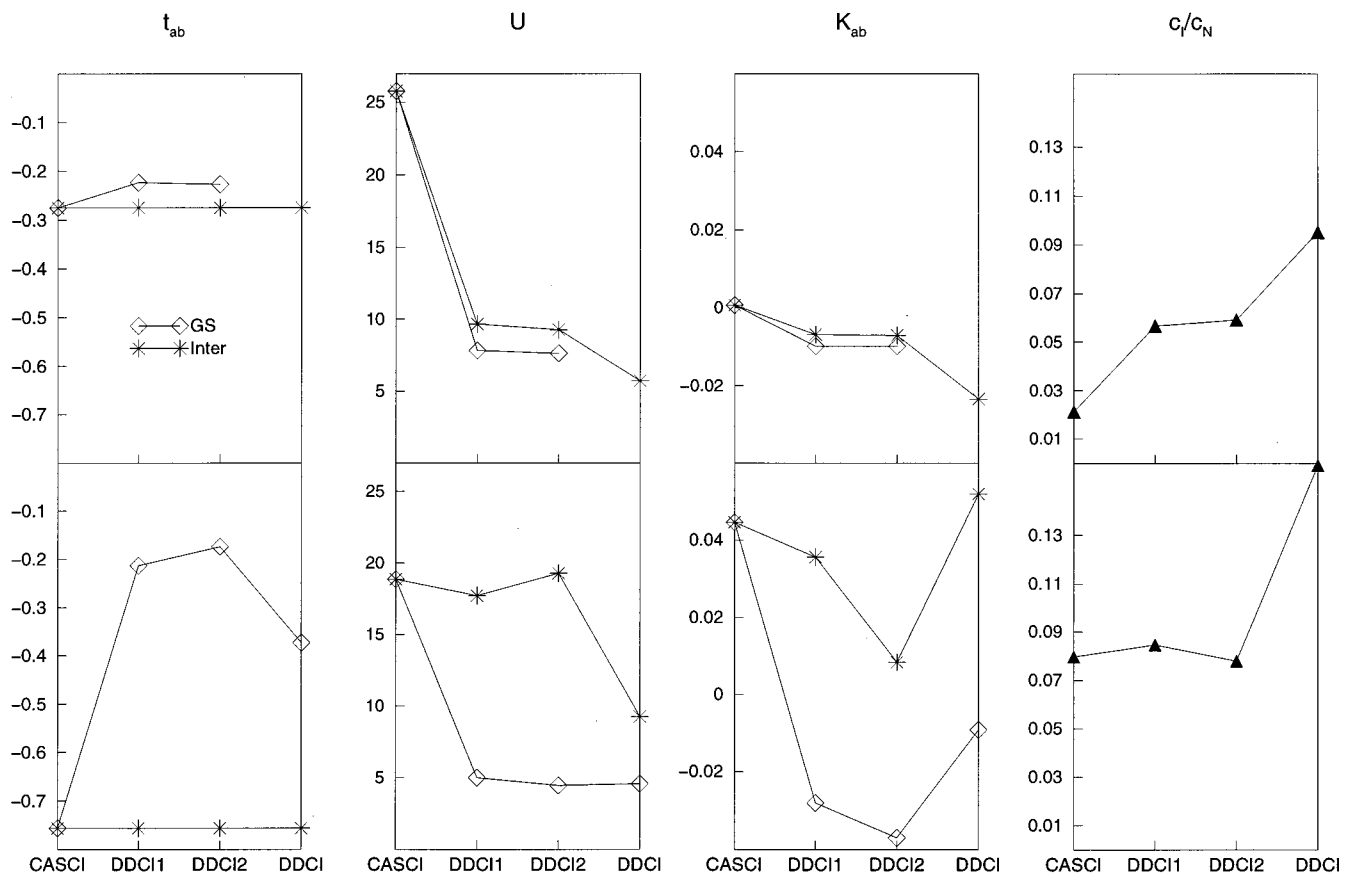
TABLE III. Magnetic coupling (J), ionic/neutral ratio of the ground state (c_I/c_N), and effective parameters (t_{ab}, K_{ab}, and U) for the $[Cu_2(\mu\text{-}N_3)_2(NH_3)_6]^{2+}$ complex. For the CI calculations, the CASCI and DDCI lists of determinants have been employed, with two sets of orbitals (ROHF and natural orbitals). The CI parameters have been obtained by using the Gram–Schmidt (GS) and the intermediate (Int) effective Hamiltonians. All values in cm^{-1}, except for U, which is in eV.

MOs	Level	J^a	c_I/c_N	H_{eff}	U	$2K_{ab}$	t_{ab}
ROHF	CASCI	−82	0.021		25.77	12	−2218
	DDCI	−802	0.095	Int	5.73	−380	−2218
Natural	CASCI	−253	0.080		18.85	720	−6100
	DDCI	−1103	0.159	GS	4.57	−147	−3007
				Int	9.27	837	−6100
B3LYP		−3026	0.341		3.26	−144	−4482

$^a J_{\text{exp}}$: <-800 cm^{-1}, from Ref. 44.

FIG. 4. Effective parameters t_{ab}, K_{ab}, and U (in eV) and ionic/neutral ratio (c_I/c_N) in the ground state wave function obtained for the $[\text{Cu}_2(\mu\text{-N}_3)_2(\text{NH}_3)_6]^{2+}$ complex from increasingly correlated CI wave function. The Gram–Schmidt and intermediate effective Hamiltonians have been used and two different sets of molecular orbitals, ROHF (on the top) and natural orbitals (on the bottom), have been considered.

$$(H_{II} - E_k)c_I^k + \sum_{L \neq I \in S} H_{IL}c_L^k + \sum_{\alpha \notin S} H_{I\alpha}c_\alpha^k = 0, \qquad (45)$$

where

$$|\Psi_k\rangle = \sum_{L \in S} c_L^k |L\rangle + \sum_{\alpha \notin S} c_\alpha^k |\alpha\rangle \qquad (46)$$

and

$$H_{IL} = \langle I|\hat{H}|L\rangle \quad \text{and} \quad H_{I\alpha} = \langle I|\hat{H}|\alpha\rangle. \qquad (47)$$

The state specific energy shift of the diagonal matrix element may be defined for each determinant of the model space:

$$\Delta_{II}^k = \left(\sum_{\alpha \notin S} H_{I\alpha}c_\alpha^k \right) (c_I^k)^{-1}, \qquad (48)$$

which from Eqs. (43) and (44) gives

$$\hat{P}_S(\hat{H} + \hat{\Delta}^k)\hat{P}_S|\hat{P}_S\Psi_k\rangle = E_k|\hat{P}_S\Psi_k\rangle. \qquad (49)$$

This strategy may be applied to the present problem. Taking the energy of the triplet as the reference, ^3E_u, we ask the intermediate Hamiltonian to reproduce the energy of the neutral singlet state $|^1\Psi_g^1\rangle$ and the corresponding ratio c_I/c_N of the valence purely ionic and purely neutral states in it. In this symmetry the model space is bidimensional, spanned by $|S_g^N\rangle$ and $|S_g^I\rangle$, and the energy of the lowest root $|^1\Psi_g^I\rangle$ with respect to the triplet state is

$$^1E_g^1 - {}^3E_u = 2K_{ab}^{\text{Int}} + \frac{U^{\text{Int}} - \sqrt{(U^{\text{Int}})^2 + 16t_{ab}^2}}{2}$$

[see Eq. (16) of paper I[35]].   (50)

In this basis set the intermediate Hamiltonian is

$$\begin{array}{c} |S_g^N\rangle \\ |S_g^I\rangle \end{array} \begin{vmatrix} 2K_{ab}^{\text{Int}} & 2t_{ab} \\ 2t_{ab} & U^{\text{Int}} + 2K_{ab}^{\text{Int}} \end{vmatrix}, \qquad (51)$$

where t_{ab} has been forced to keep the bare valence value. Solving the secular equations the c_I/c_N ratio can be written

$$\frac{c_I}{c_N} = \frac{U^{\text{Int}} - \sqrt{(U^{\text{Int}})^2 + 16t_{ab}^2}}{4t_{ab}}. \qquad (52)$$

The effective parameters follow the relations

$$2K_{ab}^{\text{Int}} = (^1E_g^1 - {}^3E_u) - 2t_{ab}\frac{c_I}{c_N},$$

$$U^{\text{Int}} = 2t_{ab}\frac{c_I^2 - c_N^2}{c_I c_N}. \qquad (53)$$

In terms of the coefficients of the symmetry-adapted determinants, λ and μ, the effective parameters in the intermediate Hamiltonian can be expressed as

TABLE IV. Magnetic coupling (J), ionic/neutral ratio of the ground state (c_I/c_N), and effective parameters (t_{ab}, K_{ab}, and U) for the $Cu_2(\mu\text{-}CH_3COO)_4(H_2O)_2$ molecule. For the CI calculations, the CASCI and the DDCI lists of determinants have been employed, with two sets of orbitals (ROHF and natural orbitals). The CI parameters have obtained by using the Intermediate (Int) Hamiltonian. All values in cm^{-1}, except for U, which is in eV.

MOs	Level	J^a	c_I/c_N	U	$2K_{ab}$	t_{ab}
ROHF	CASCI	-19	0.011	23.72	4	-1042
	DDCI	-195	0.049	5.19	-92	-1042
Natural	CASCI	-33	0.025	19.84	66	-1996
	DDCI	-238	0.066	7.49	25	-1996
B3LYP		-557	0.103	3.94	-216	-1645

$^a J_{exp}$: -286 cm^{-1}, -294 ± 4 cm^{-1}, from Refs. 45 and 46.

$$2K_{ab}^{Int} = ({}^1E_g^1 - {}^3E_u) - 2t_{ab}\frac{\lambda - \mu}{\lambda + \mu},$$

$$U^{Int} = -8t_{ab}\frac{\lambda\mu}{\lambda^2 - \mu^2}. \tag{54}$$

2. Results

The intermediate Hamiltonian interactions appear in Tables I–IV and Figs. 2–5 for the four systems. Let us first comment the results from ROHF MOs:

(i)   The effective exchange K_{ab}^{Int} may be significantly different from its bare value and its sign may become negative (as occurs in three of the systems at the DDCI level).

(ii)   The on-site repulsion U^{Int} is again considerably reduced with respect to the CASCI value, essentially under the effect of $1h+1p$ determinants, but now the antiferromagnetic effect of the $2h+1p$ and $1h+2p$ determinants results in an additional reduction of U^{Int} since t_{ab} is kept fixed. The DDCI final values of U^{Int} (5–7 eV) are in qualitative agreement with the U^{GS} values previously discussed (Tables I–IV). The cuprate fragment has the largest value of U^{Int}, which can be interpreted as due to the fact that the O^{-2} ligand is less polarizable than those of the other systems.

When going to NOs, the starting CASCI t_{ab} values are much larger. The ratio $t_{ab}^{Natural}/t_{ab}^{ROHF}$ varies between 1.4 for Cu_2O_7 to 2.75 for the azido complex. This variation results from the
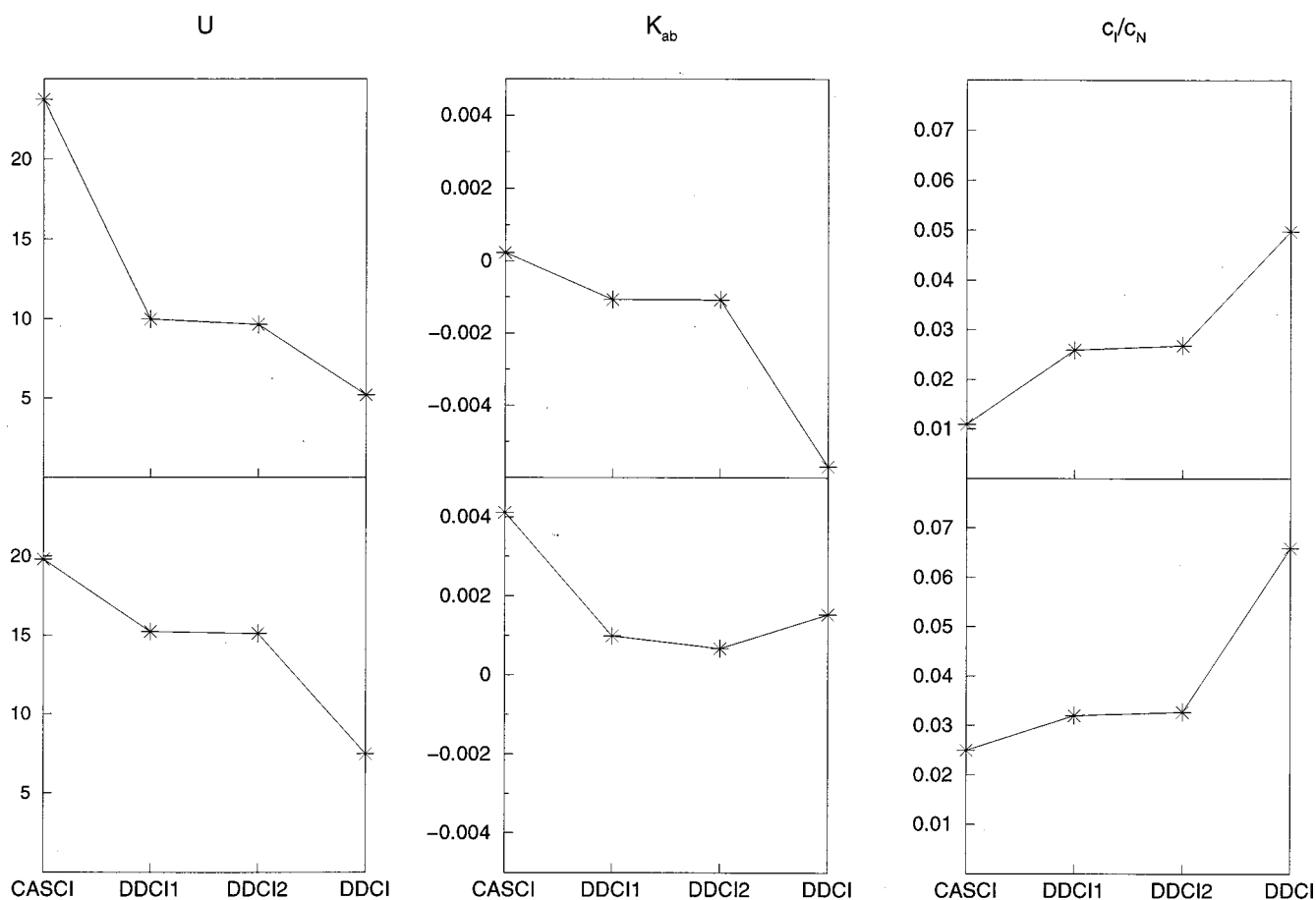

FIG. 5. Effective parameters t_{ab}, K_{ab}, and U (in eV) and ionic/neutral ratio (c_I/c_N) in the ground state wave function obtained for the $Cu_2(\mu\text{-}CH_3COO)_4(H_2O)_2$ molecule from increasingly correlated CI wave function and by using an intermediate effective Hamiltonian, and with two different sets of molecular orbitals: ROHF (on the top) and natural orbitals (on the bottom).

much larger delocalization of the NOs. The change of the c_I/c_N ratio under the effect of the dynamical correlation (CASCI versus DDCI values) is much weaker from NOs than from ROHF MOs. This is consistent with the larger delocalization tails of the natural magnetic orbitals. Since $c_I/c_N \sim 2|t_{ab}|/U$, the variation of U^{Int} for NOs is significantly smaller. The CASCI value of U^{Int} is smaller than for ROHF orbitals (effect of the delocalization) and the final DDCI value of U^{Int} ranges from 7.5 eV for the acetato complex to 10 eV for the cuprate fragment. As another consequence of the delocalization in the NOs, the K_{ab}^{Int} value is much larger at the CASCI level and it remains large at the DDCI level.

D. Comparison between different effective Hamiltonians

Three types of effective Hamiltonians have been considered in this section. The most informative one is the Bloch Hamiltonian, which handles three energy differences and two eigenvectors but which is not Hermitian. Sacrificing the information about the ionic singlet state of g symmetry, the Hermiticity is restored in the Gram–Schmidt version. Losing all knowledge on the ionic states and using only the singlet-triplet energy difference and the neutral singlet eigenvectors leads to the intermediate effective Hamiltonian.

The use of the Bloch Hamiltonian is not recommended in view of its violent non-Hermiticity, reflected in the values of t_{NI}^B and t_{IN}^B (Table I). The hopping integrals obtained from the Gram–Schmidt procedure by using the ROHF MOs are quite similar to the bare CASCI values. This supports the intermediate Hamiltonian formalism which keeps t_{ab} fixed at its bare value. The results obtained with the NOs are less stable.

The values of the effective direct exchange K_{ab} depend on the choice of the procedure and of the molecular orbitals. The main and common feature of all procedures and all MO sets is the dramatic reduction of the effective on-site repulsion U.

From a practical point of view, we would recommend the use of the intermediate Hamiltonian procedure which does not require the rather difficult identification of the ionic excited states in the CI spectrum.

IV. EFFECTIVE VALENCE INTERACTIONS FROM DFT CALCULATIONS

A. Theory

Some attempts have been reported[16–18] to establish a connection between the DFT calculations and the usual valence-only descriptions which are formulated in terms of three parameters, K_{ab}, t_{ab}, and U, or K_{ab}, $(\varepsilon_g - \varepsilon_u)$, and $(J_{aa} - J_{ab})$ [Eqs. (10) and (11), respectively]. Inconsistencies appear in the proposed procedures (the extracted K_{ab}, t_{ab}, and U values are not consistent with the calculated J value),[16] which can be related with the difficulties in defining the proper singly-occupied molecular orbitals (SOMOs) in the broken-symmetry calculations. The present article pro-

poses an alternative extraction, after a careful definition of the SOMOs. The procedure involves the variational calculation of three states:

(i)   the unrestricted triplet state $|T_{UHF}^+\rangle = |gu\rangle$;
(ii)   the unrestricted broken-symmetry solution $|S^{BS}\rangle = |a^{BS}\bar{b}^{BS}\rangle$; and
(iii) the closed-shell singlet state $|S_{g\bar{g}}\rangle = |g\bar{g}\rangle$.

From the first calculation, after a proper definition of the α-SOMOs[62] (for instance, by using the NOs given in GAUSSIAN or those obtained from some projection technique), it is possible to extract a relevant t_{ab} value:

$$2t_{ab}^{\text{DFT}} = \varepsilon_g^{\text{SOMO}} - \varepsilon_u^{\text{SOMO}}, \tag{55}$$

where $\varepsilon_g^{\text{SOMO}}$, $\varepsilon_u^{\text{SOMO}}$ are the orbital energies. Since $|T_{UHF}^+\rangle = |gu\rangle = |ab\rangle$, the energy of the triplet state can be written as

$$E_{T_{UHF}^+} = \langle ab|\hat{H}|ab\rangle = \langle a\bar{b}|\hat{H}|a\bar{b}\rangle - K_{ab}^{\text{DFT}}. \tag{56}$$

The energy of the closed-shell singlet can be expressed easily since

$$|g\bar{g}\rangle = \tfrac{1}{2}(|a\bar{b}\rangle + |b\bar{a}\rangle + |a\bar{a}\rangle + |b\bar{b}\rangle), \tag{57}$$

$$E_{S_{g\bar{g}}} = \tfrac{1}{2}(\langle a\bar{b}|\hat{H}|a\bar{b}\rangle + \langle a\bar{a}|\hat{H}|a\bar{a}\rangle) + K_{ab}^{\text{DFT}} + 2t_{ab}^{\text{DFT}}. \tag{58}$$

Following Eq. (28) and considering $K'_{ab} = K_{ab}$, $\langle a\bar{a}|\hat{H}|a\bar{a}\rangle = \langle a\bar{b}|\hat{H}|a\bar{b}\rangle + U$, hence

$$E_{S_{g\bar{g}}} = \langle a\bar{b}|\hat{H}|a\bar{b}\rangle + \frac{U^{\text{DFT}}}{2} + K_{ab}^{\text{DFT}} + 2t_{ab}^{\text{DFT}}. \tag{59}$$

The broken-symmetry solution leads to the definition of two nonorthogonal orbitals a^{BS} and b^{BS}. When $|t_{ab}^{\text{DFT}}/U^{\text{DFT}}| \ll 1$, these two orbitals can be expressed perturbatively as

$$a^{BS} = a - \frac{t_{ab}^{\text{DFT}}}{U^{\text{DFT}}}b, \quad b^{BS} = b - \frac{t_{ab}^{\text{DFT}}}{U^{\text{DFT}}}a. \tag{60}$$

The broken-symmetry determinant can be developed as

$$S^{BS} = |a^{BS}\bar{b}^{BS}\rangle$$
$$= |a\bar{b}\rangle - \frac{t_{ab}^{\text{DFT}}}{U^{\text{DFT}}}(|a\bar{a}\rangle + |b\bar{b}\rangle) + \left(\frac{t_{ab}^{\text{DFT}}}{U^{\text{DFT}}}\right)^2 |b\bar{a}\rangle. \tag{61}$$

Its energy may be identified to the low-order expression, provided that $|t_{ab}^{\text{DFT}}/U^{\text{DFT}}|$ is small enough, and hence $\langle a^{BS}|b^{BS}\rangle = -2t_{ab}^{\text{DFT}}/U^{\text{DFT}}$:

$$E_{S_{BS}} = \langle a\bar{b}|\hat{H}|a\bar{b}\rangle - \frac{2(t_{ab}^{\text{DFT}})^2}{U^{\text{DFT}}}. \tag{62}$$

Equation (56) gives the hopping integral and from Eqs. (56), (59), and (62), the effective interactions K_{ab}^{DFT} and U^{DFT} can be extracted:

$$E_{S_{g\bar{g}}} - E_{T_{UHF}^+} = 2t_{ab}^{\text{DFT}} + \tfrac{1}{2}U^{\text{DFT}} + 2K_{ab}^{\text{DFT}}, \tag{63}$$

$$E_{S_{BS}} - E_{T_{UHF}^+} = -\frac{2(t_{ab}^{\text{DFT}})^2}{U^{\text{DFT}}} + K_{ab}^{\text{DFT}}. \tag{64}$$

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Equation (65) is consistent with the recommendation[63,64] to evaluate the coupling constant, J, in the density functional approach as $J = 2(E_{S_{BS}} - E_{T_{UHF}^+})$.

B. Results

As shown elsewhere,[62] the DFT magnetic orbitals are much more delocalized than the ROHF ones and significantly more delocalized than the natural magnetic orbitals. If they were used with the exact Hamiltonian, according to the trend observed when going from ROHF MOs to NOs, very large increases of $|t_{ab}|$ and K_{ab} and a lowering of U would be expected. Actually the DFT energies are obtained with a modified exchange, and the effective DFT parameters are quite different from the values they would have using the exact Hamiltonian. Since the overlap between the magnetic orbitals a^{BS} and b^{BS} in the broken-symmetry solution is quite small in all the studied systems ($S_{ab}^{\alpha\beta} = 0.12$ for the chloride complex, 0.29 for the azido complex, 0.23 for the cuprate, and 0.11 for the acetato complex), the B3LYP parameters have been calculated according to the above-described procedure. They are reported in Tables I–IV together with the calculated J values, always exceedingly antiferromagnetic. One can see that

(i)   the K_{ab}^{DFT} value is far from being negligible, its sign may be negative (cf. Tables III and IV);

(ii) the $|t_{ab}^{DFT}|$ value is smaller than the bare value of $|t_{ab}|$ for the NOs, despite the larger delocalization tails of the DFT magnetic orbitals.[62] A certain underestimation of the hopping integrals in DFT calculations with respect to the best CI calculations have been noticed in mixed-valence compounds[65,66] in the recent past;

(iii) the U^{DFT} effective on-site repulsion is exceedingly low, half of the values obtained from the *ab initio* effective Hamiltonians, in particular for the chloride.

As a result, the $|2t_{ab}^{DFT}/U^{DFT}|$, i.e., the c_I/c_N ratio, is too large. DFT exaggerates the ionic component of the wave function, i.e., the fluctuation or the intermetallic delocalization in the singlet state.

As previously discussed,[63,67] this effect is entirely due to the exchange potential. Actually, by increasing the amount of Fock exchange without changing the correlation part of the original B3LYP functional in the cuprate, Fig. 6 shows that $|t_{ab}^{DFT}|$ and K_{ab}^{DFT} are slightly reduced, but U^{DFT} is dramatically increased and of course the c_I/c_N ratio is reduced. For the mixing giving the experimental J value for this system, $|t_{ab}^{DFT}|$ and U^{DFT} remain slightly smaller than the values obtained from the *ab initio* effective Hamiltonian ($t_{ab}^{DFT} = -0.48$ eV, $t_{ab}^{GS} = -0.507$ eV, $U^{DFT} = 6.4$ eV, $U^{GS} = 7.3$ eV). The c_I/c_N ratio becomes 0.150 with this mixing of the exchange functionals, close to the *ab initio* value of 0.136 eV. The reduction of $|t_{ab}^{DFT}|$ and K_{ab}^{DFT} and the increase of U^{DFT} when increasing the Fock part of the hybrid exchange are consistent with the trend to reduce the ligand content of the DFT magnetic orbitals, observed and discussed elsewere.[62]
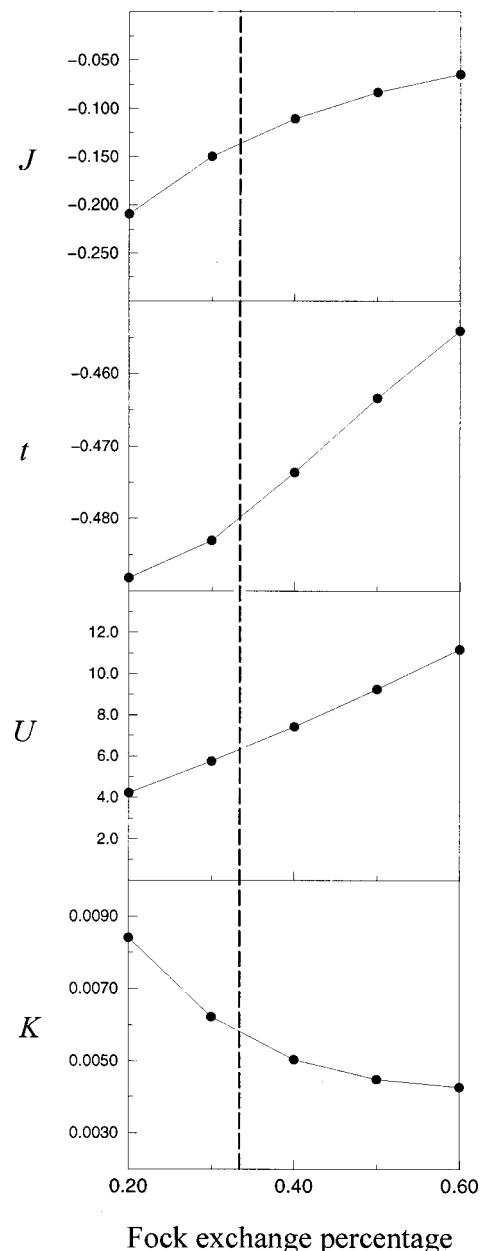

FIG. 6. Effect of the Fock exchange percentage used in the exchange functional on the values of the magnetic coupling J and the effective parameters t_{ab}, K_{ab}, and U for the La_2CuO_4 system. All the values in eV. The dashed vertical line corresponds to the Fock percentage recovering the experimental J value.

V. CONCLUSIONS

Most of the qualitative interpretations of the magnetic coupling in binuclear complexes are based on very limited valence-only spaces, with two electrons in two magnetic orbitals. The model handles three basic parameters: the direct exchange, K_{ab}, the hopping integral, t_{ab}, and the on-site Coulombic repulsion, U. When using the exact Hamiltonian and a variational definition of the magnetic orbitals, either ROHF MOs or NOs, the valence-only CI calculations produce unreliable values of the magnetic coupling J. The values of J have sometimes an incorrect sign and in antiferromagnetic systems the amplitude of J is frequently one order of magnitude too small. From these CI matrices, the values

of on-site repulsion, U, are much larger (>20 eV) than what is usually assumed in model Hamiltonians. As was shown, accurate values of J are only obtained when the complex dynamical correlation effects are taken into account. From this contrast it might be concluded that it is impossible to project the physics of the coupling onto a valence picture, as do most of the qualitative models.

The present article shows that it is possible to extract from sophisticated extended CI calculations effective valence-only Hamiltonians, in which the effective interactions K_{ab}, t_{ab}, and U are completely revised under the effect of the nonvalence determinants. Three procedures have been proposed. The most refined one, the Bloch development, has the defect of being non-hermitian, leading to different values for the neutral to ionic and ionic to neutral hopping integrals. This problem is avoided through an appropriate Gram–Schmidt orthogonalization of the eigenvectors. These two methods require the identification of four eigenstates with large projections on the valence model space. The identification is not difficult for the two lowest, mostly neutral, eigenstates ($|^1\Psi_g^1\rangle, |^3\Psi_u\rangle$), but it can be quite arbitrary for the intermetallic charge transfer states, which are strongly mixed with the LMCT states.

A third, less demanding, definition has been proposed using the theory of the intermediate Hamiltonians, which only uses the energies of the two lowest states and the wave function of the singlet state, conserving the value of t_{ab} obtained from the bare valence CASCI. This simplification is supported by the final value of t_{ab} obtained from the Gram–Schmidt effective Hamiltonian, which turns out to be close to the bare t_{ab} value.

Whatever the definition of the effective Hamiltonian, it may be concluded that the main effects of the dynamical correlation are the following:

(i)   The effective direct exchange K_{ab} integral is affected by the dynamical correlation, which may change its sign. Due to the larger delocalization tails of the NOs, the corresponding K_{ab} is more positive than when working with ROHF MOs. However, its value is strongly dependent on the procedure followed and a univocal determination of K_{ab} has not been possible.

(ii)   The effective U value ($U \sim 5-8$ eV) is dramatically reduced from its bare value, being divided by a factor between 3 and 4. This reduction is essentially due to the dynamical polarization of the ionic VB structure since it appears at the DDCI1 level. This reduction results in a considerable increase of the ionic VB component of the ground singlet state (c_I/c_N ratio is multiplied by a factor between 2 and 5).

Regarding the DFT approaches, the present article shows that it is possible to extract from different solutions of the Kohn–Sham equations, consistent values of the three parameters K_{ab}, t_{ab}, and U:

(i)   although slightly underestimated, the t_{ab} value is in good agreement with the *ab initio* estimates;

(ii)   the effective exchange K_{ab} may be negative, probably due to spin polarization effects, incorporated in the UHF and broken-symmetry solutions;

(iii)   the effective on-site repulsion U is exceedingly small, between 2 and 4 eV. This underestimation of U has been shown to be due to the exchange potential and it is consistent with both the systematic overestimation of the antiferromagnetic coupling and the observed exceedingly delocalized character of the magnetic orbitals.[62] The excess of the ionic component of the singlet wave function is consistent with the underestimation of the DFT spin-densities in ferromagnetic systems.

The two papers of this series have

(i)   shown once more the irrelevance of bare valence description;

(ii)   confirmed the possibility to obtain accurate values of the magnetic coupling provided that the state specific dynamical correlation effects are properly treated, as done by the DDCI technique;

(iii)   demonstrated the possibility to analyze the various types of dynamical correlation effects (spin polarization, dynamical polarization of VB ionic components, dispersive contribution to the effective hopping) and to assess their order of magnitudes (i.e., to combine numerical accuracy with intelligibility);

(iv)   explained why dynamical correlation increases the ligand/metal delocalization (phenomenologically observed elsewhere[62]);

(v)   shown the possibility to return, in a rational and controlled manner to a valence-only picture, the main effect of the dynamical correlations consisting in a drastic reduction of the on-site electronic repulsion U;

(vi)   proposed consistent handling of DFT calculations for the definition of the magnetic orbitals and the derivations of the DFT K_{ab}, t_{ab}, and U parameters; and

(vii)   systematically confronted the best *ab initio* correlated descriptions to the DFT ones, showing that the most widely used approximation of the exchange functional (B3LYP) dramatically underestimated U, which results in an overestimation of the charge fluctuation and of the antiferromagnetic coupling.

ACKNOWLEDGMENTS

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eration, through the integrated action HF2000-30. The Laboratoire de Physique Quantique is Unité Mixte de Recherche (UMR 5626) du CNRS.

APPENDIX: THIRD-ORDER QDPT CONTRIBUTIONS TO THE HOPPING INTEGRAL

It is possible to analyze the leading QDPT third-order contributions to the effective Hamiltonian. Let us call $\Delta \hat{H}^{(3)}$ the correction, given by

$$\langle I|\Delta \hat{H}^{(3)}|J\rangle = \sum_{\alpha \notin S} \sum_{\beta \notin S} \frac{\langle I|\hat{H}|\alpha\rangle\langle\alpha|\hat{H}|\beta\rangle\langle\beta|\hat{H}|J\rangle}{(E_J^{(0)}-E_\alpha^{(0)})(E_J^{(0)}-E_\beta^{(0)})}$$
$$- \sum_{\alpha \notin S} \sum_{K \in S} \frac{\langle I|H|\alpha\rangle\langle\alpha|H|K\rangle\langle K|H|J\rangle}{(E_J^{(0)}-E_\alpha^{(0)})(E_K^{(0)}-E_\alpha^{(0)})}.$$

(A1)

Most of the contributions to these two terms are *unlinked* and cancel. One must concentrate on the *linked* contributions to the second term of Eq. (A1) and especially those that couple the ionic and the neutral model space determinants. They involve excitations that act differentially on the ionic and the neutral determinants, and especially the large effect of the $1h+1p$ excitations on the ionic ones. In the second summation, a large contribution is expected when $|I\rangle=|a\bar{a}\rangle=|K\rangle$ and $|J\rangle=|a\bar{b}\rangle$ or $|J\rangle=|b\bar{a}\rangle$:

$$\langle a\bar{a}|\Delta H^{(3)}|b\bar{a}\rangle = -\sum_{\alpha \notin S} \frac{\langle a\bar{a}|H|\alpha\rangle\langle\alpha|H|a\bar{a}\rangle\langle a\bar{a}|H|b\bar{a}\rangle}{(E_{a\bar{b}}^{(0)}-E_\alpha^{(0)})(E_{a\bar{a}}^{(0)}-E_\alpha^{(0)})},$$

(A2)

where $E_{a\bar{b}}^{(0)}$ and $E_{a\bar{a}}^{(0)}$ are the energies of the neutral and the ionic VB determinants, respectively. When $\{|\alpha\rangle\}$ are the $1h+1p$ determinants, one may write

$$\langle a\bar{a}|\Delta \hat{H}^{(3)}|b\bar{a}\rangle = -\sum_h^{\text{occ}} \sum_p^{\text{vir}} \frac{\langle h|\breve{J}_a-\breve{J}_b|p\rangle^2 t_{ab}}{(U+\Delta E_{h\to p})(\Delta E_{h\to p})},$$

(A3)

where $\breve{J}_a = \frac{1}{2}(\hat{J}_a - \hat{K}_a)$. This contribution decreases the amplitude of t_{ab}. If a closure approximation on the $h\to p$ excitation energies is performed,

$$\Delta E_{h\to p} = \overline{\Delta E}_{h\to p} \quad \forall h,p,$$

(A4)

Eq. (A3) can be written

$$\langle a\bar{a}|\Delta \hat{H}^{(3)}|b\bar{a}\rangle = t_{ab}\left(\frac{\Delta U}{\overline{\Delta E}_{h\to p}}\right),$$

(A5)

where ΔU is the large negative change $\Delta U=U^{\text{eff}}-U$ of the on-site repulsion due to the $1h+1p$ determinants defined in Eq. (13). Hence the $(1h+1p)$ determinants decrease the amplitude of the $\langle a\bar{a}|H^{\text{eff}}|b\bar{a}\rangle$ interaction. However, the matrix element $\langle b\bar{a}|\hat{H}^{\text{eff}}|a\bar{a}\rangle$ will not be affected by such an effect since there is not significant linked contribution to

$$\langle b\bar{a}|\Delta H^{(3)}|a\bar{a}\rangle = -\sum_{\alpha \notin S} \frac{\langle b\bar{a}|H|\alpha\rangle\langle\alpha|H|b\bar{a}\rangle\langle b\bar{a}|H|a\bar{a}\rangle}{(E_{a\bar{b}}^{(0)}-E_\alpha^{(0)})(E_{a\bar{a}}^{(0)}-E_\alpha^{(0)})}.$$

(A6)

The QDPT theory leads to the Bloch non-Hermitian effective Hamiltonian if it converges. The present Appendix explains why the Bloch effective Hamiltonian matrix elements verify

$$|\langle a\bar{a}|H_{\text{Bloch}}^{\text{eff}}|b\bar{a}\rangle| < |\langle b\bar{a}|H_{\text{Bloch}}^{\text{eff}}|a\bar{a}\rangle|,$$

(A7)

as observed in the results of the Bloch Hamiltonian section.

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